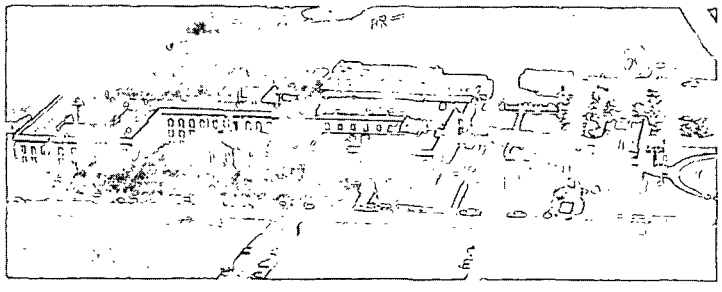

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STUDIES ON POLYMORPHY IN CELLULOSE

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INTRODUCTION

This publication is the extended abstract of a paper prepared for presentation at the Canadian Wood Chemistry Symposium, September 1-3, 1976. It provides an overview of our investigations of polymorphy in cellulose which have utilized, for the first time, significant new information from Raman spectral studies of native, mercerized, and regenerated celluloses. Some of the basic insights developed in this work guide our efforts to control and/or modify the supermolecular structure of pulp fibers and, thereby, their properties.

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ABSTRACT

Our Raman spectral studies of the different polymorphic forms of cellulose have led us to conclude that the cellulose molecule can exist in either of two highly ordered states which can be represented as relatively small left and right-handed departures from the commonly accepted twofold helix structure. The two ordered states have distinctive characteristic spectra which occur separately or in combination in the spectra of all polymorphic variants. This presentation will cover the bases for our conclusions concerning the states of cellulose, as well as our interpretation of polymorphic variation in terms of these states.

The major differences between the Raman spectra of cellulose I and cellulose II occur in the region below 600 cm^{-1} which is dominated by the skeletal bending and torsion modes; the spectra have very few features in common in this region. In contrast, many features are unchanged in the region above 800 cm^{-1} where the dominant modes are the skeletal stretching and the methine, methylene, and hydroxyl bending motions. The differences between the spectra of celluloses I and II have been interpreted in terms of two stable ordered conformations, each with its distinctive spectrum, after consideration of a number of lines of evidence:

(a) Published calculations of the conformational potential energy show surfaces with multiple minima. When the additional constraints of a repeat length of approximately 5.15 A per anhydroglucose unit and an intramolecular hydrogen bond O---O separation between 2.5 and 2.8 A are added, two minima, representing both left and right handed departures from the twofold helix, appear to be the likely locii of stable conformations.

(b) A theoretical analysis of the effect of changes in the dihedral angles at the glycosidic linkage showed that the primary effects are to be expected in the skeletal bending region, and that the skeletal stretching modes are altered to a much more limited degree.

(c) The Raman spectra of the polymorphs of amylose and of its cyclic oligomers, where the differences in conformation are more clearly defined, show their most significant differences in the same region as the differences between celluloses I and II.

(d) Raman spectra of solutions of cellulose show the greatest departure from the spectra of celluloses I and II in the region characteristic of the bending modes.

The analyses of conformational potential energy, when taken together with observations of the spectra of many polymorphic variants, suggest that only two ordered conformations are stable and that these are the departures from the twofold helix noted above. This interpretation of the spectra of celluloses I and II has provided a basis for the

use of Raman spectroscopy to complement x-ray diffractometry in studies of polymorphy in cellulose, and has made possible the development of new insights into the processes of mercerization and regeneration.

The studies of mercerization had two objectives, namely, to explore the nature of the changes in molecular order which result from the lattice conversion, and to clarify the mechanism whereby the changes are brought about. Only results related to the first of the two objectives will be considered in this presentation. The essence of the work was to expose samples of highly crystalline cellulose to mercerizing solutions of different strength, and monitor the magnitude of change with x-ray diffractometry and Raman spectroscopy. The x-ray diffractograms appeared to be superimpositions of the diffractograms of celluloses I and II, in proportion to the degree of conversion. The Raman spectra also were combinations of the spectra of celluloses I and II, and were taken as evidence for conversion of molecular chains from one of the stable conformations to the other. Taken together the x-ray diffractograms and the Raman spectra of the partially converted samples indicate that some crystalline domains have been converted in both conformation and lattice type, while others have remained in the native form.

In the studies on regeneration, x-ray diffractometry and Raman spectroscopy were used to explore the structures of celluloses precipitated from the dimethylsulfoxide-para-formaldehyde (DMSO-PF) solvent system and from phosphoric

acid both fairly soon after dissolution and after a period of weeks to permit significant reduction in the degree of polymerization (DP). In all three series the temperatures of regeneration ranged up to 180°C.

The celluloses regenerated from the DMSO-PF system and from phosphoric acid fairly soon after dissolution showed approximately the same range of polymorphic variation with temperature of regeneration. The x-ray diffractograms were typical of cellulose II for samples regenerated at or below room temperature. As the temperature was increased to 60°C the celluloses became more crystalline, though the form remained a cellulose II. At 100°C the cellulose was recovered as a mixture of II and IV, at 130°C as a low crystallinity IV, and at 160-170°C as a cellulose IV of fairly high crystallinity.

The celluloses recovered after approximately three weeks in phosphoric acid showed a wider range of polymorphic variation over the same temperature range. At room temperature a highly crystalline cellulose II was formed. At 100°C substantial conversion to cellulose IV was observed, although a small residue of II was present. At 140°C no residue of II was found, only a highly ordered IV. Ultimately at 160°C a highly crystalline cellulose I was recovered.

The Raman spectra of the regenerated samples reflect the variations in polymorphic form, but the pattern of

the spectral changes does not permit a simple correlation with the x-ray diffractometric indices of polymorphic form. The most remarkable feature is that the spectra of samples which produce distinct cellulose IV diffractograms are essentially the same as the spectra of the partially mercerized celluloses which are mixtures of the I and II polymorphs. These observations are representative of many others wherein the spectra of cellulose IV samples have been examined; they have been interpreted as evidence that conformations I and II coexist in the cellulose IV polymorph. When the distinctive x-ray diffractograms of cellulose IV samples are considered as well it seems most plausible that the cellulose IV polymorph represents a mixed crystalline habit in which both conformations coexist.

Though the effects of temperature are in part modified by the mechanics of regeneration and the DP of the cellulose, certain clear patterns emerge. As the temperature of regeneration is raised above a certain level, which is determined in part by DP, an increasing proportion of the cellulose chains separate in the I conformation. These seem to coprecipitate with molecular chains separating in the II conformation, giving rise to a fraction of the total precipitate in the IV form, while the rest of the precipitate remains the II polymorph. As the temperature is increased further, or the DP lowered, a much larger proportion of the molecular chains separate as a coprecipitate of conformations I and II in the IV polymorph. At higher temperatures

still, the IV polymorph dominates and there is no evidence for separate precipitation of the II polymorph. Ultimately, for a low enough DP and 160°C the molecular chains separate entirely in the I conformation and the crystalline form is that of the native cellulose I state.

Yet another effect of temperature on molecular order has been observed. For samples of cellulose I or II of relatively low crystallinity, exposure to elevated temperatures, in media which tend to swell cellulose, was found to increase the level of order. The changes are most clearly manifested in a narrowing of the profiles of the various reflections in the x-ray diffractograms. These effects have been interpreted in analogy with annealing phenomena well known in thermoplastics and usually associated with an increase in the long period characteristic of crystalline order in such polymers.

The results of the studies outlined above, among others, have led us to seek a simple and concise manner for representing the state of order of a cellulosic chain. A method based on the two stable states of the glycosidic linkage suggests itself; these two states correspond to values of the dihedrals defining the small left- and right-handed departures from the twofold helix, designated as L and R, respectively. These then permit use of a framework analogous in concept to the one used to describe order in other classes of polymeric systems. In such a framework, pure celluloses I and II would be identified as R

or L homopolymers, while the partially mercerized celluloses and cellulose IV would be viewed as block copolymers which give rise to different space lattices. Amorphous cellulose could then be viewed as a random copolymer. This framework for describing order in cellulose chains appears to be a suitable basis for quantitative analysis of some of the data on polymorphic variation.

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